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THERMAL CHARACTERISTICS OF 3501-6/AS AND 5208/T300 GRAPHITE EPO--ETC(U)

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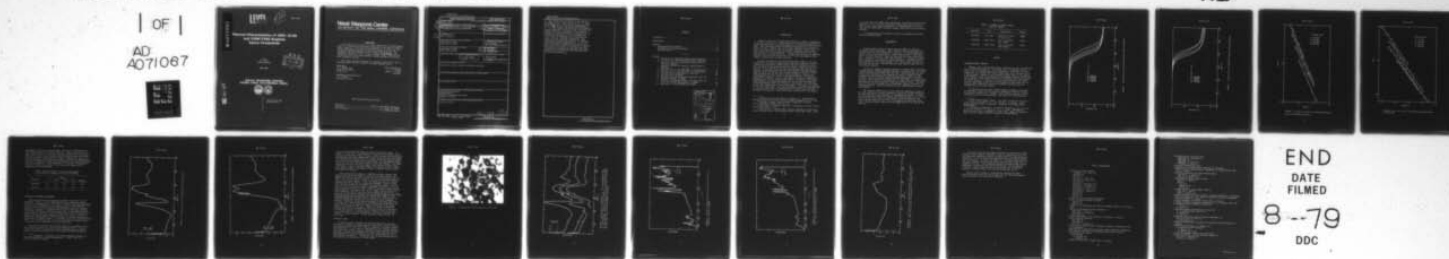
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# Thermal Characteristics of 3501-6/AS and 5208/T300 Graphite Epoxy Composites

by  
R. F. Kubin  
Research Department

MAY 1979

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### FOREWORD

This report is the result of a study conducted at the Naval Weapons Center to investigate the sustained combustion of two types of graphite epoxy composites. This research was performed by the author for the Systems Survivability Branch. The work was funded under Air Task Assignment A03P-03PA/008C/8W-0592-001, element number 63514N. The sponsoring official was Cdr. E. Lewis of NavAir 03PAJ. This work was carried out during the period February through September 1978 and has been informally reported.

This report has been reviewed for technical content by Dr. Karl C. Kauffman and Dr. Albert H. Lepie of the Naval Weapons Center.

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(U) *Thermal Characteristics of 3501-6/AS and 5208/T300 Graphite Epoxy Composites*, by R. F. Kubin. China Lake, Calif., Naval Weapons Center, May 1979. 18 pp. (NWC TP 6104, publication UNCLASSIFIED.)

(U) The thermal characteristics of two graphite epoxy composites for use as aircraft structural components have been investigated. The activation energies and heats of reaction for pyrolysis of the composites were found to be 19.7 kcal/mole and -18.4 cal/g for 3501-6/AS and 25.0 kcal/mole and -20.4 cal/g for 5208/T300, respectively. The kinetic parameters enable prediction of thermal degradation at flight temperatures. In fire fighting, bulk material temperatures must be reduced well below 300°C to prevent continuation of exothermic pyrolysis reactions. It was also found that differential scanning calorimetry provides a more sensitive test of composite cure than reflectance infrared measurements. ↙

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## INTRODUCTION

Composite materials have been fabricated into a number of components of aircraft structures.<sup>1-3</sup> These materials offer distinct advantages in weight reduction and strength improvement over conventional metal construction. These advantages become increasingly important in the design of V/STOL aircraft. However, the use of these composite materials has also meant the introduction of some technological problems, some of which have not been fully characterized. In this latter group are the fire characteristics of these materials. As newer aircraft use more composite materials (the F-18 uses on the order of 2/3 ton), knowledge of these thermal characteristics becomes important.

Testing undertaken at the Naval Weapons Center (NWC) on the fire survivability of certain graphite epoxy composites revealed a problem.<sup>4</sup> A sample was subjected to a destructive fire then quenched by either water or Purple K (potassium bicarbonate,  $\text{KHCO}_3$ ). Carbon dioxide ( $\text{CO}_2$ ) was found to be ineffective; the fire would reflash when the  $\text{CO}_2$  was removed. Thermocouple data from the test specimens indicated interior temperatures of the 1/2-inch and 3/4-inch samples in the 300 to 320°C range at quench and the test was considered complete. However, the instrumentation was left on and it was discovered that the interior temperatures continued to rise to over 480°C. This was a reproducible phenomenon and the fire fighting implications are obvious. This phenomenon suggests a possible deep-seated fire not entirely quenched with standard techniques and/or an exothermic reaction able to be initiated by the 300°C thermal mass of the test specimen. The answer is a combination of both hypotheses. Thus one implication is that fire fighting must be continued until material temperatures are reduced well below 300°C throughout the material. While 300°C would be quite hot to our senses,

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<sup>1</sup> Charles F. Bersch and Luther B. Lockhart, Jr., "Navy Composite Materials Research," *National Defense* (November-December 1977), p. 220.

<sup>2</sup> Fredrick H. Immen, "Army Helicopter Composites," *National Defense* (November-December 1977), p. 224.

<sup>3</sup> Frank Cherry, "Advanced Composites in Aerospace," *National Defense* (March-April 1978), p. 474.

<sup>4</sup> John Fontenot, "Graphite Epoxy Composite Response in Pool Fires," Project Progress Report, Naval Weapons Center, China Lake, Calif., 1978.

it is well below the 1000°C skin temperatures of the self-sustained epoxy composite fire<sup>4</sup> or the 1400°C and hotter flame temperatures in fires. Thus the fire might appear quenched but the remaining heat content at 300°C may be sufficient to initiate burning, which could lead to reflash problems.

A limited program was initiated to study the phenomenon and determine the probable cause.

## EXPERIMENTAL

Thermal analysis offers a rapid, sensitive means of initially analyzing composite materials. All studies in this initial phase were carried out in an inert atmosphere of nitrogen. The thermogravimetric analyses (TGA) were carried out on a Perkin Elmer Model 1. The differential scanning calorimetry (DSC) work was done on a DuPont 990 instrument. Samples for use on the DSC were prepared in a nitrogen atmosphere and encapsulated in hermetically sealed containers. Nitrogen gas was used to purge the DSC furnace during a run. The nitrogen flow rate was 40 cc/min for all runs. The TGA runs were made using an open cup in a well-purged apparatus.

In order to identify pyrolysis products a reaction vessel containing a thermocoupled, insulated platinum crucible was constructed. The vessel could be evacuated and purged with inert gas. Combustion products were carried from the vessel by the purge gas to traps to perform a rough separation of gases evolving from room temperature to 400°C and >400 to 800°C. These traps were isolated from the atmosphere by a CaSO<sub>4</sub> drying tower and a one-way valve using water, in that order, to prevent back diffusion of air into the product traps and pyrolysis vessel. The duration of this project allowed only a qualitative analysis of some of the reaction products. These were analyzed by gas chromatography and mass spectrometry.

The composite samples used in this study are summarized in Table 1. For these composites the epoxy compound is N,N,N',N'-tetraglycidylmethylethane dianiline and the curing agent is diaminodiphenylsulfone. In order to have consistent sample size several sections from each of the 1/2-inch and 15/16-inch sheets were cut and turned to 1/8-inch diameter rods. These rods were then cut into 15 to 20 mg samples and each face filed flat to improve thermal contact with the sample pans for the DSC and TGA analyses.



TABLE 1. Summary of Graphite Epoxy Composite Samples.

Material	Size	Fabrication	Source
5208/T300	1/2" sheet	300°F for 3 hours no post cure	AMMRC
5208/T300	.040" sheet	Post cured 400°F for 4 hours	HITCO
3501-6/AS	15/16" sheet	Post cured 350°F for 8 hours	HITCO

## RESULTS

## THERMOGRAVIMETRIC ANALYSES

Figures 1 and 2 show normal pyrolytic behavior for both the 3501-6/AS and the 5208/T300 composites. The weight loss is an apparent smooth function of the heating rate for both composites. There was an initial weight loss up to around 320°C which ranged from 0.5% to not quite 3% in a random manner. Because of the preparation method used for the samples, their identity as far as distance from the original composite surface was not determined. This initial weight loss was thought to be water based on several reports.<sup>5,6</sup> However, a series of mass spectral data taken over the temperature range 50 to 175°C revealed not only water but, increasing with temperature, molecular fragments associated with the decomposition of the resin matrix.

The TGA data were put into a simple computer program to calculate the activation energy for the pyrolysis assuming an Arrhenius form for the specific reaction rate. Figures 3 and 4 show the results of these calculations for the two composites. The line fits to the data were

<sup>5</sup> Naval Surface Weapons Center. *The Effect of Moisture Sorption in a Real Outdoor Environment*, by J. M. Augl and A. E. Berger. Silver Spring, Maryland, NSWC, 14 June 1977. (NSWC TR 77-13, publication UNCLASSIFIED.)

<sup>6</sup> University of Minnesota. *Structural Inelasticity. XIX. A Review of Moisture Diffusion in Composites*, by P. K. Sinka. Minneapolis, Minnesota, University of Minnesota, January 1978. (Dept. of Aerospace Engr. and Mech. Report AEM-H1-19, publication UNCLASSIFIED.)

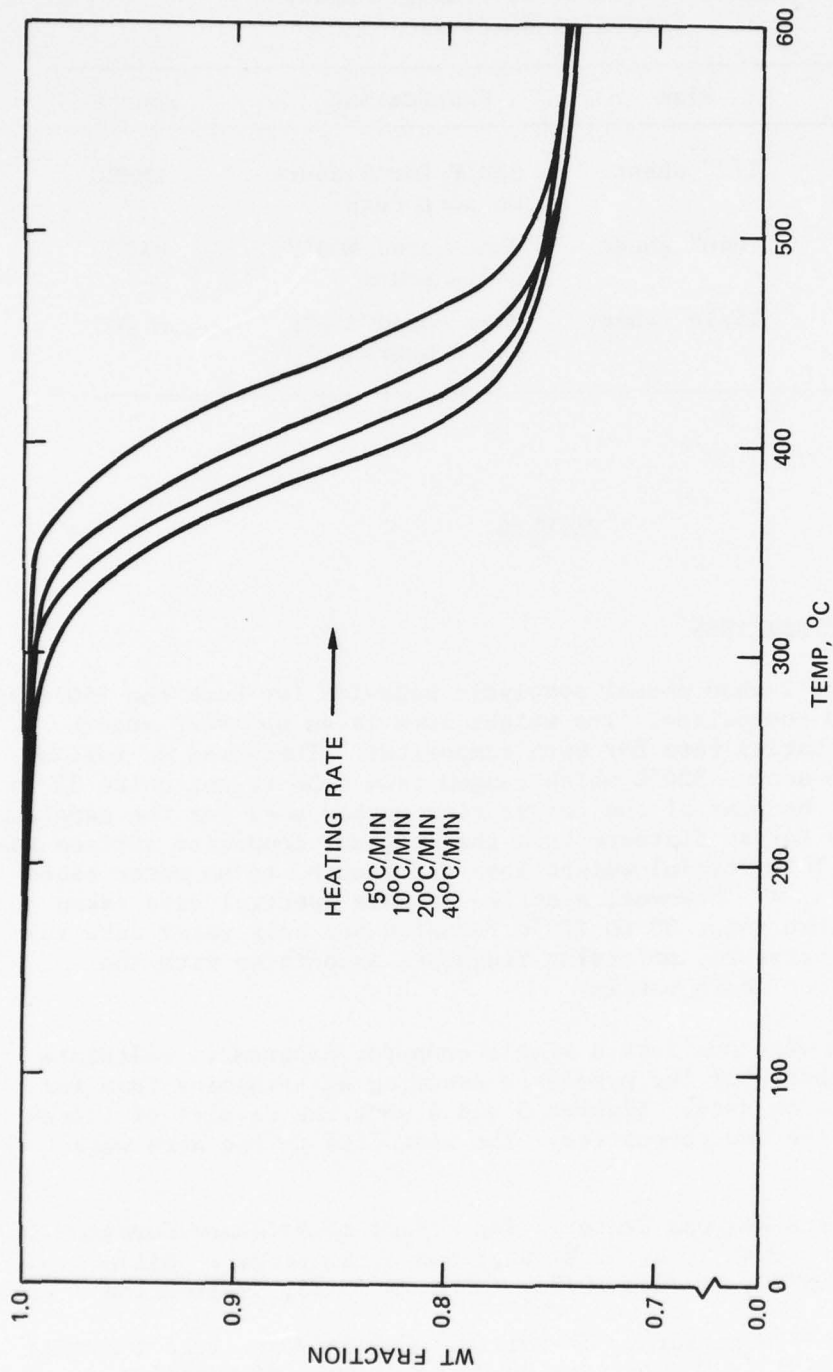


FIGURE 1. TGA Curves for 3501-6/AS Graphite Epoxy Composite.

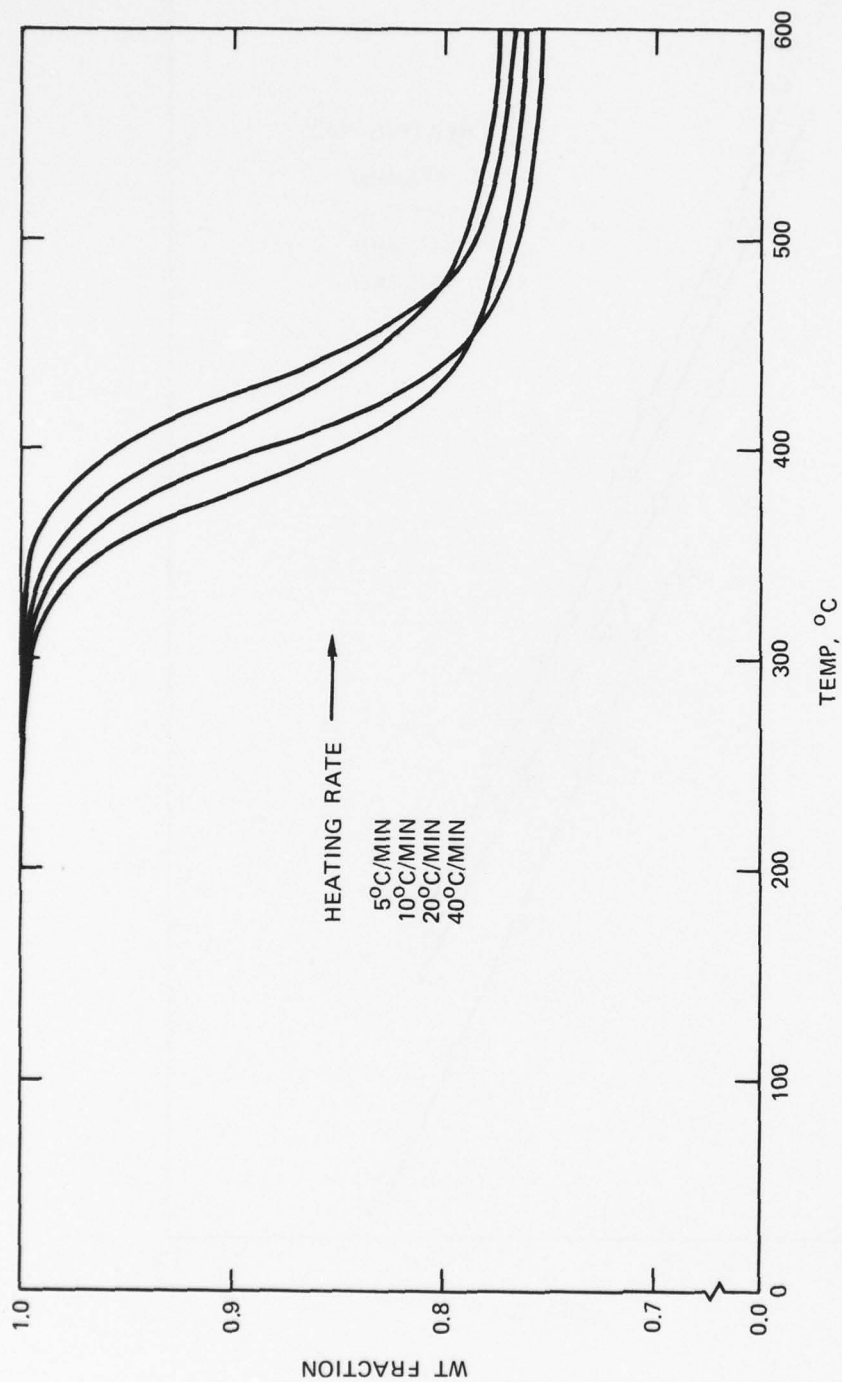


FIGURE 2. TGA Curves for 5208/T300 Graphite Epoxy Composite.

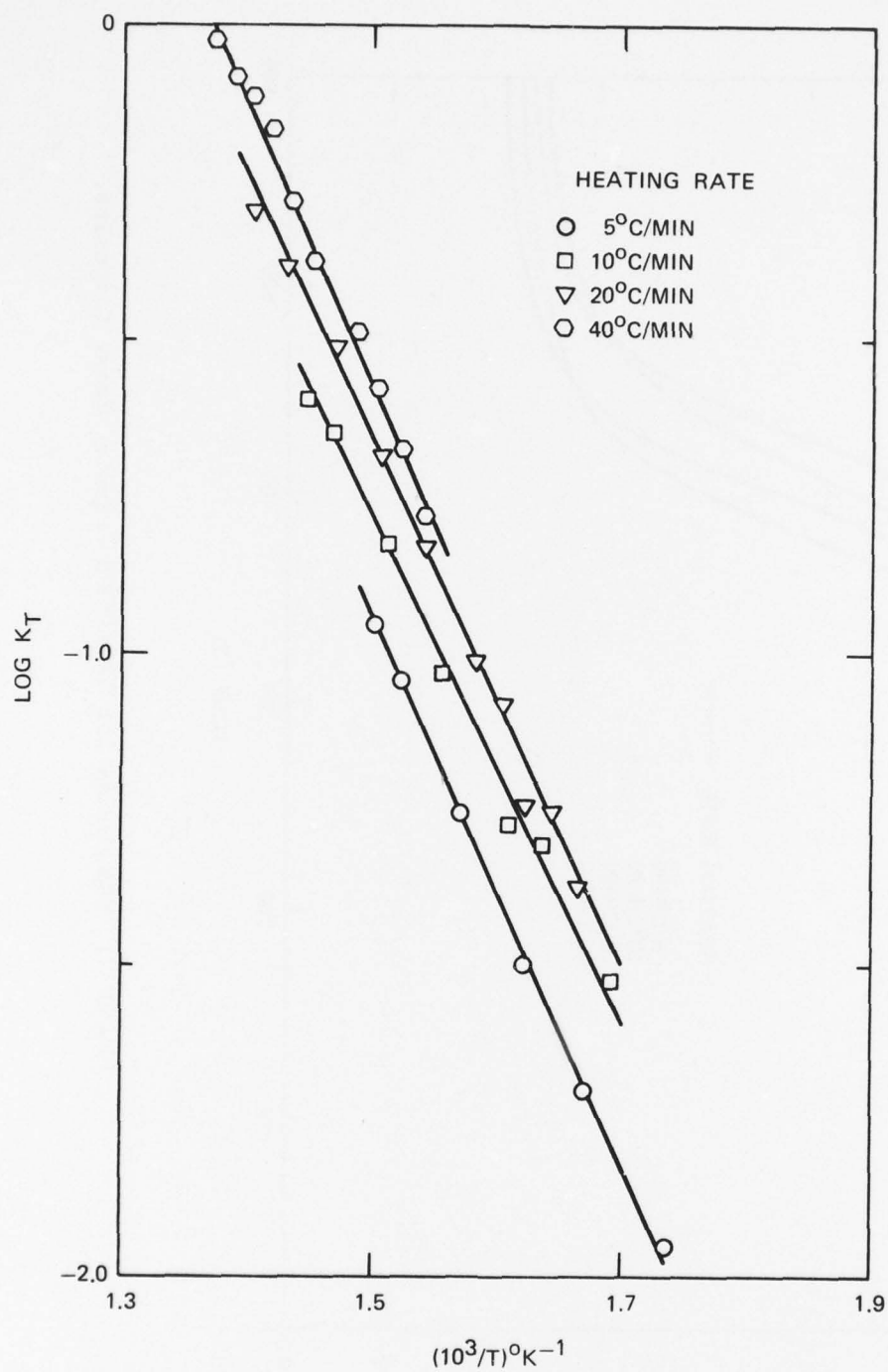


FIGURE 3. Log  $K_T$  vs  $(10^3/T)$  for Different Heating Rates of 3501-6/AS Composite.



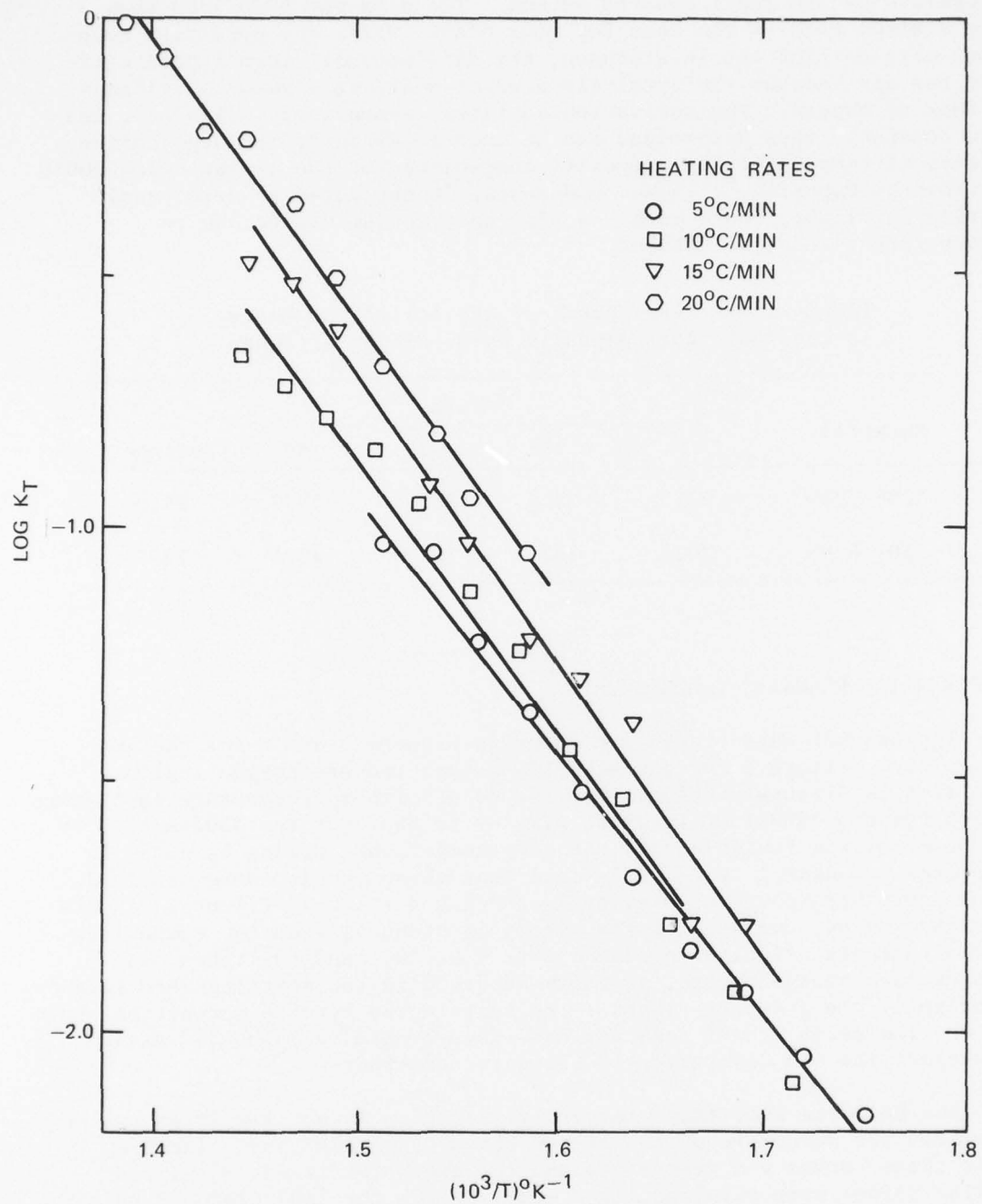


FIGURE 4. Log  $K_T$  vs  $(10^3/T)$  for Different Heating Rates of 5208/T300.

determined by the least squares method. The data for 5208/T300 show more scatter than do the data for 3501-6/AS. While the pyrolysis reactions were carried out in nitrogen, the data probably form a good estimate for air because the pyrolysis product analyses showed no evidence of lack of oxygen. The activation energies, summarized in Table 2, and rate constants thus determined can be used to estimate the degradative effects of temperature on composite components for the region below 200°C as shown by Papazian.<sup>7</sup> These components, if subjected to aerodynamic heating in flight, could suffer a slow progressive damage due to temperature rise above ambient.

TABLE 2. Observed Values of the Activation Energy in kcal/mole for Composite Pyrolysis in Nitrogen.

Material	°C/min.				Average
	5	10	20	40	
5208/T300	23.3	25.1	26.4	25.2	25.0
3501-6/AS	20.2	18.6	19.3	20.6	19.7

#### DIFFERENTIAL SCANNING CALORIMETRY

Typical DSC data traces are shown in Figures 5 and 6 for the two composites. Figure 5 for the 5208/T300 shows two exothermic regions. The first is discussed below. The second or higher temperature exothermic region for the 5208/T300 is quite similar to that for the 3501-6/AS. It is the pyrolysis region and is the same temperature region as noted in Reference 4. Again, it is emphasized that these results were obtained in an inert atmosphere as previously described. In experimental results described below, analyses of the pyrolysis products from the composites showed that the principal products were H<sub>2</sub>O, CO<sub>2</sub>, and CO. Thus the samples have enough oxygen, probably adsorbed in the starting materials -- principally the graphite fibers -- to sustain the pyrolysis reaction above 300°C. The resin itself does not have enough chemically bonded oxygen to support its own combustion in an inert atmosphere.

The DSC data show that the pyrolysis region is not simple as can be seen from the structure on top of the broad pyrolysis band. The area under these curves was determined and the exothermicities calculated. Similar values were obtained,  $\Delta H = -18.4$  cal/gm for 3501-6/AS and  $\Delta H =$

<sup>7</sup> H. A. Papazian. "Prediction of Polymer Degradation Kinetics at Moderate Temperatures From TGA Measurements," *J. Appl. Poly. Sci.*, Vol. 16 (1972), pp. 2503-10.

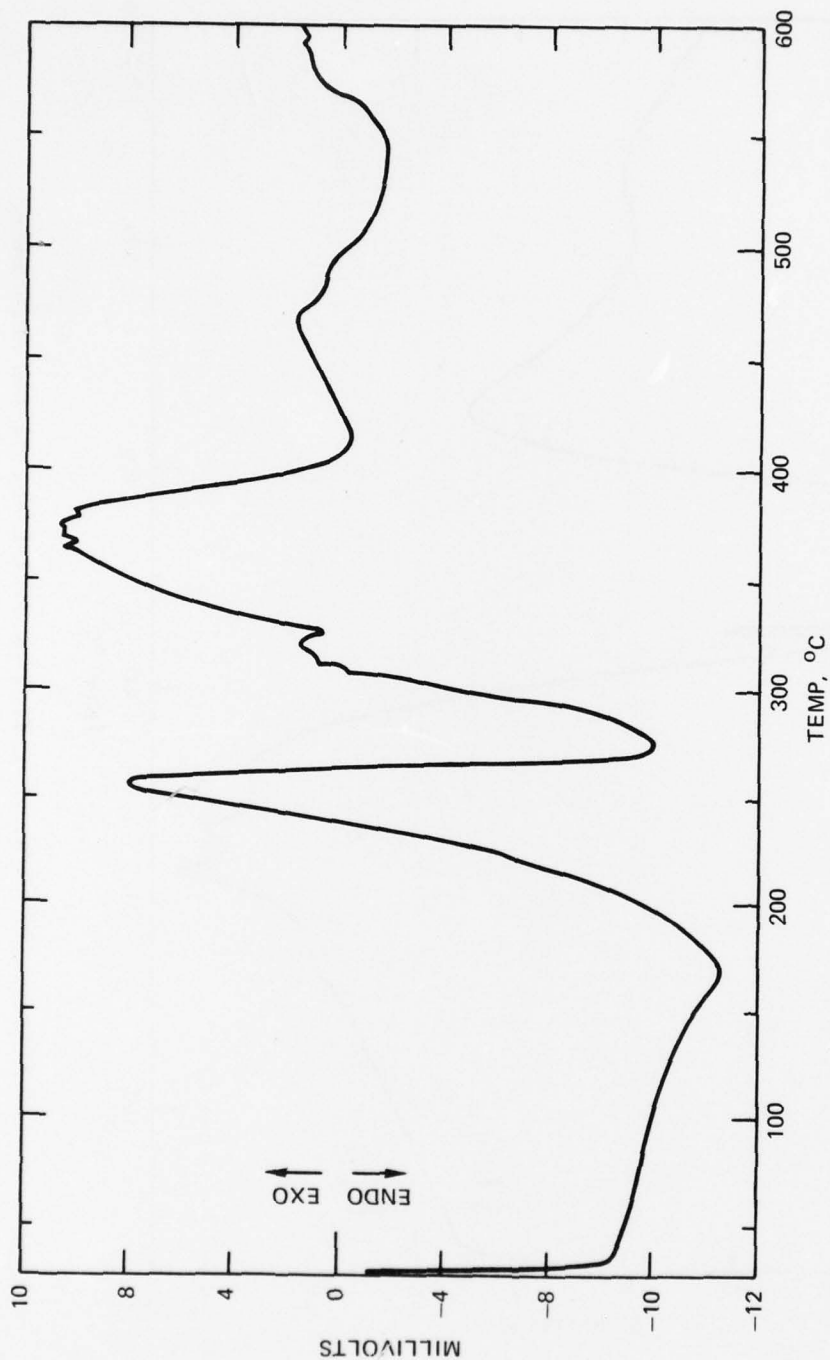


FIGURE 5. DSC Trace for 17.6 mg 5208/T300, Al Pan Reference.

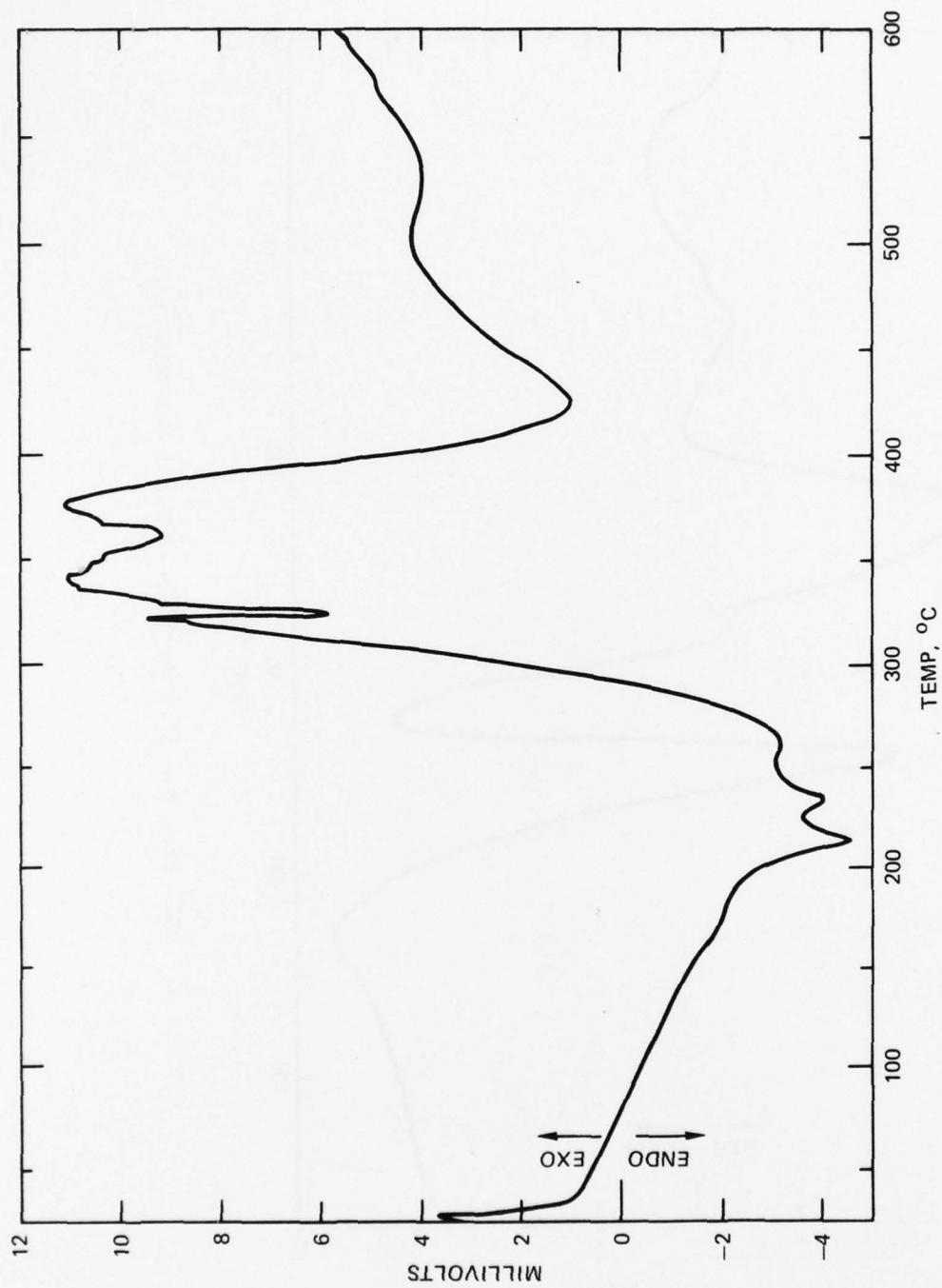


FIGURE 6. DSC Trace for 17.5 mg 3501-6/AS, Al Pan Reference.



-20.4 cal/gm for 5208/T300 based on initial total sample weight. For samples of 5208/T300, the measurement of  $\Delta H$  was made on samples cured in the DSC to essentially remove the peak at 260°C; see the discussion below. Depending upon the final temperature for the DSC or TGA runs, the weight loss varied between 20% and 30%. Two samples representing these extremes were put into the scanning electron microscope. The one sample showing only a 20% loss still had resin visible in the fiber bundles. The sample showing the 30% loss of initial weight looked like essentially clean, round dowels. Some of the fibers appear to be hollow; an end on look at one pyrolyzed sample of 3501-6/AS is shown in figure 7 where at least three holes are apparent.

With the particular sample of 5208/T300 initially supplied some question arose about the amount of curing in the resin matrix. The manufacturer gave the material no post cure and did the fabrication at 300°F. As was noted above in figure 5 there is an exothermic peak preceding the pyrolysis region. It has the characteristics of a curing reaction and could be made to essentially disappear. Figure 8 shows three DSC traces made for three nearly equal sample weights. The top trace is for a run from 25 to 600°C. The middle trace is for a run in which the sample was held at 176°C (350°F) for two hours before continuing the DSC run. The bottom trace is of a sample that was heated to 204°C (400°F) and held for one hour before completing the DSC run. In Figures 9 and 10 we have reproduced the reflectance infrared spectra taken by the Army Materials and Mechanics Research Center (AMMRC) of the 5208/T300 sample supplied this Center. Figure 9 is of the prepreg as received from Narmco. Figure 10 is of the cured 79 ply composite supplied. Figure 10 clearly shows the absence of the epoxy absorbance in the 905  $\text{cm}^{-1}$  region as well as of the NH stretching frequencies of the curing agent in the 3400  $\text{cm}^{-1}$  region, indicating a fully cured sample to the limits of detection. However, a sample of 5208/T300 manufactured by Hitco and which was post cured by them for four hours at 400°F was obtained. Its DSC trace in Figure 11 shows no exotherm in the 260°C region. Considering Figures 8 through 11 together the evidence is rather dramatic. The DSC provides a sensitive test of total cure.

#### PYROLYSIS GASES

In order to better elucidate the pyrolysis mechanism, work was initiated to identify the major products of pyrolysis. Project funding was terminated before this work could be completed. The major products identified were  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CO}$ . Additionally, the following organics were identified: ethane, propane, isopropyl alcohol, benzene, and trace propylene. Benzene so contaminated the sample collection from the gas chromatograph that positive identification of several peaks by mass spectrometry was hampered. A deliberate look for HCN revealed possible small amounts from pyrolysis of a large sample.

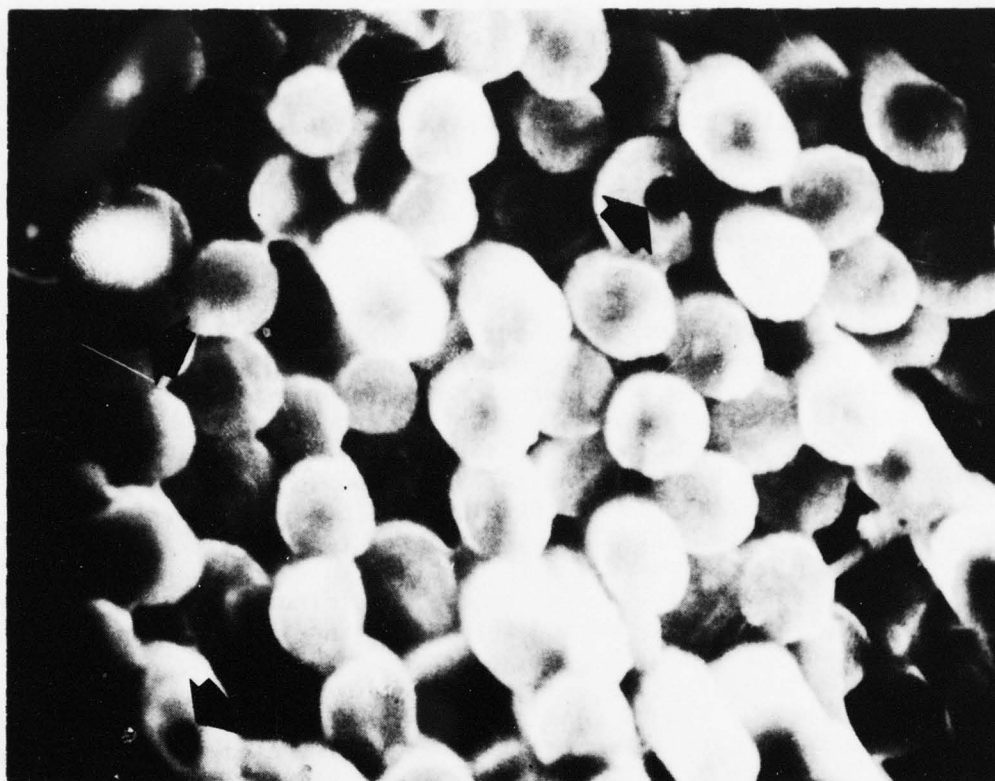


FIGURE 7. Scanning Electron Micrograph of 3501-6/AS.

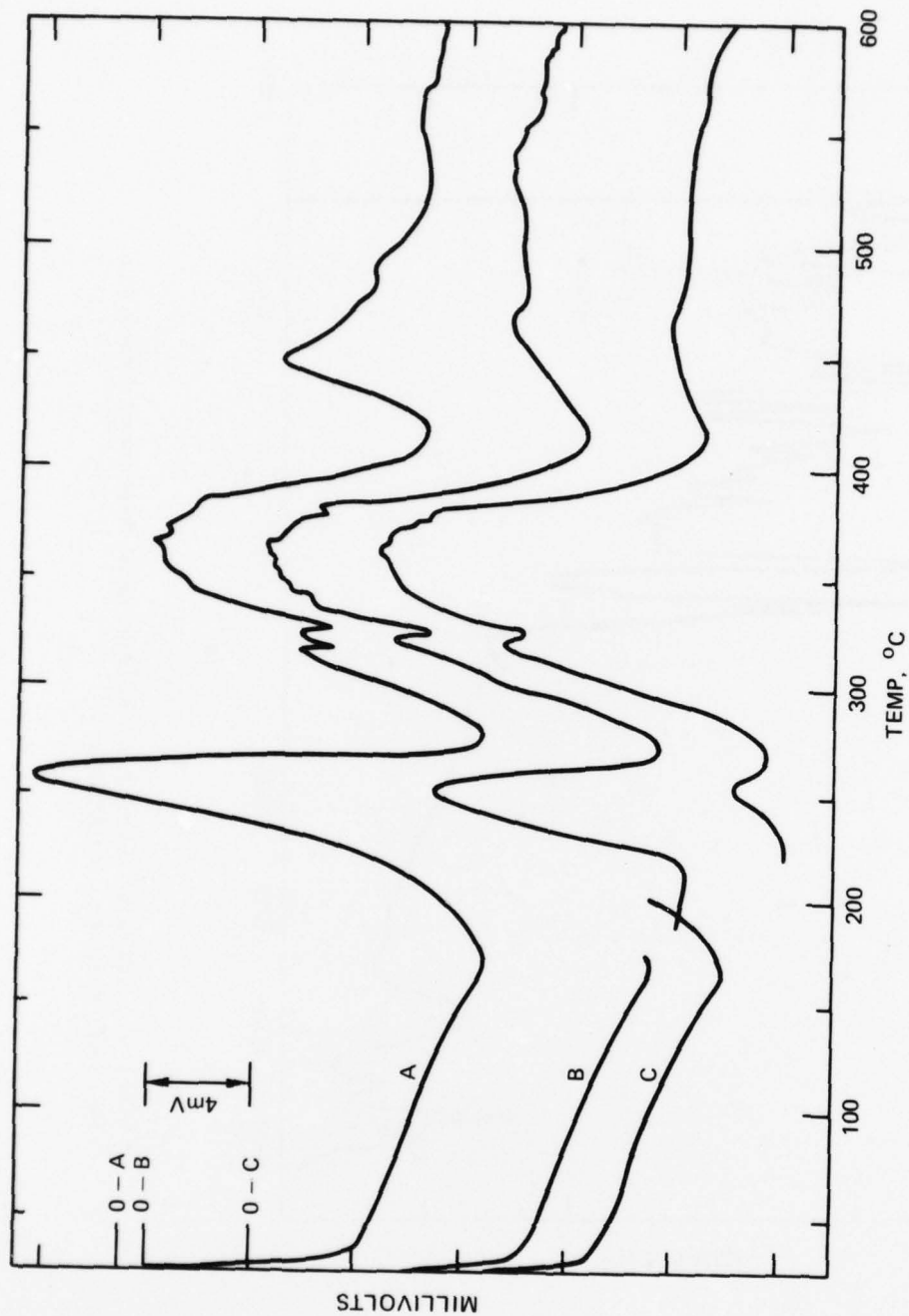


FIGURE 8. DSC Traces for 5208/T300: A. 15.0 mg Continuous DSC, B. 16.0 mg Held 2 Hours at 176°C (350°F), C. 16.5 mg Held 1 Hour at 204°C (400°F). Breaks in curves B and C were made to eliminate the transients due to the isothermal switching.

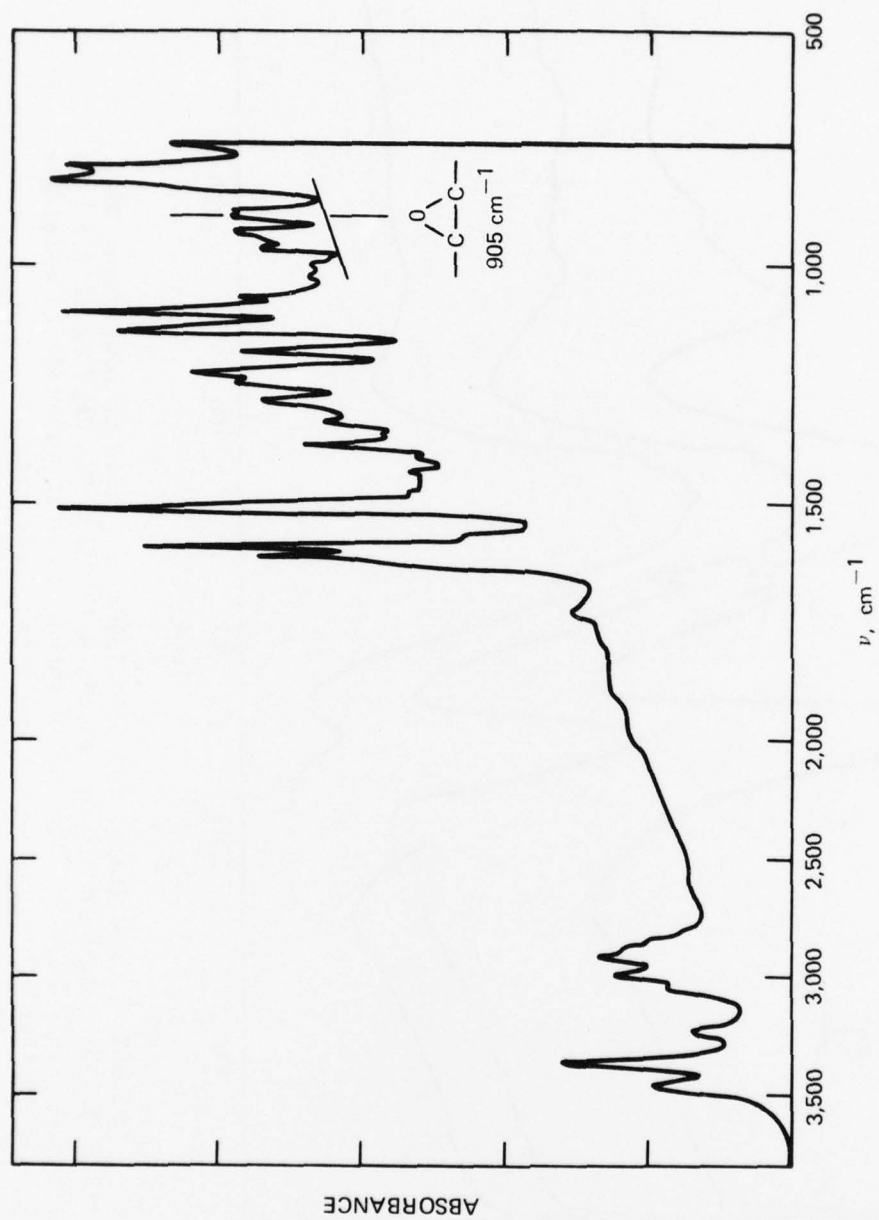


FIGURE 9. Infrared (Internal Reflectance Spectrum) Trace for 5208/T300 Prepreg, by AMRC.



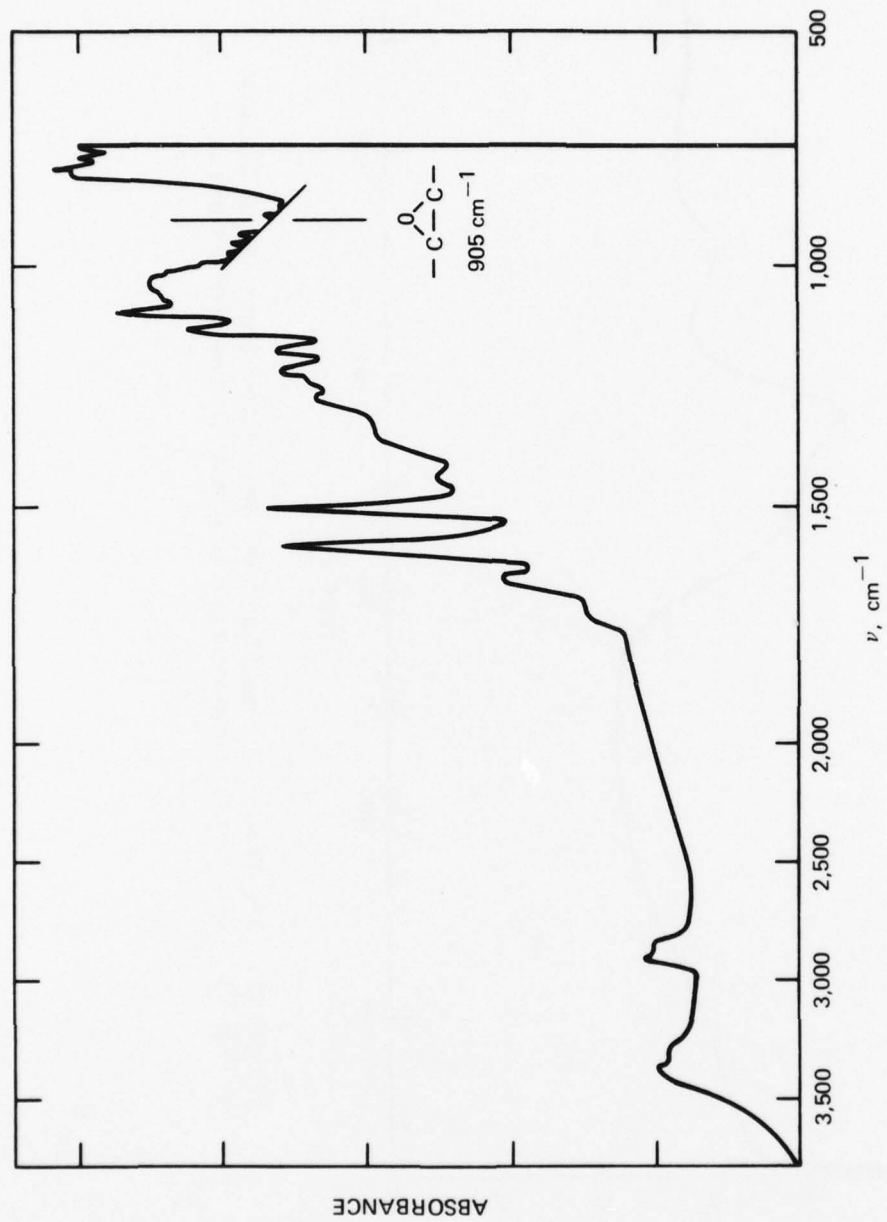


FIGURE 10. Infrared (Internal Reflectance Spectrum) Trace for Fully Cured 5208/T300 Composite, by AMMRC.

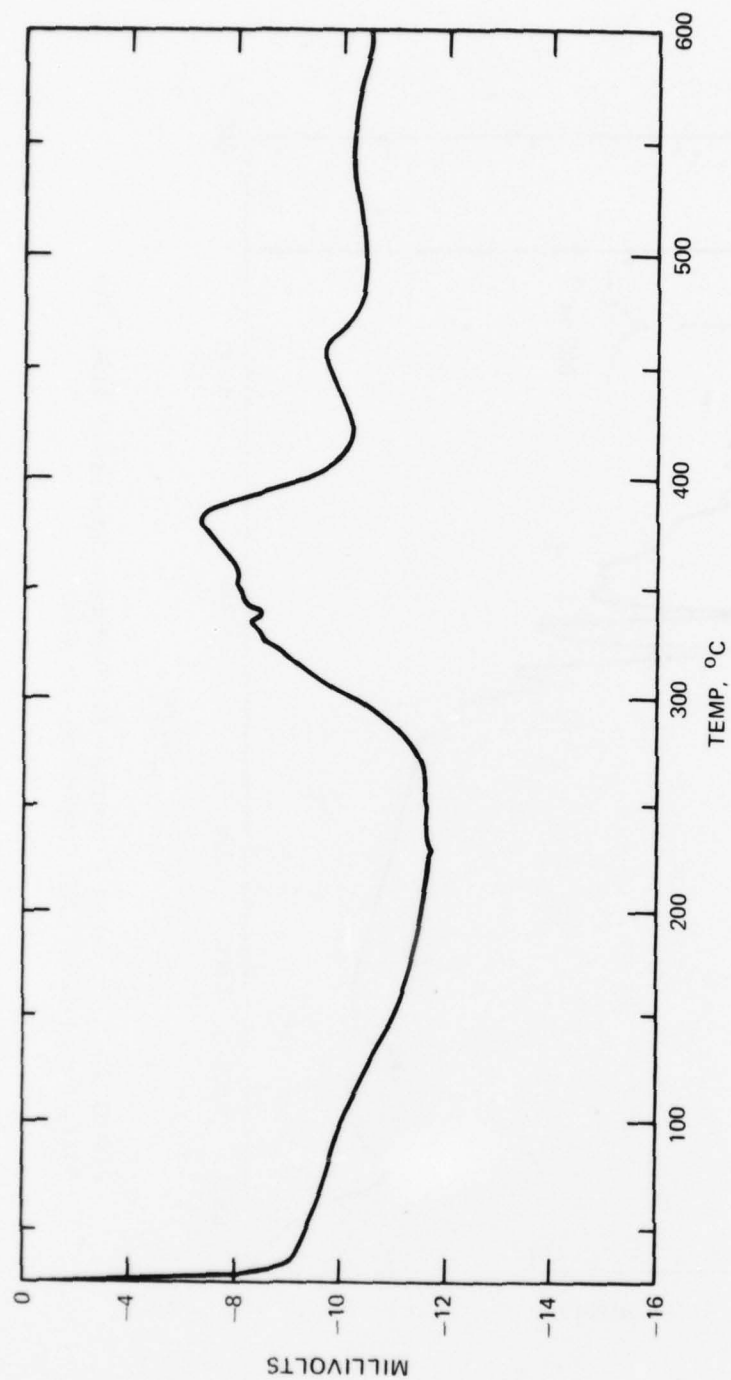


FIGURE 11. DSC Trace 15.7 mg 5208/T300 From HITCO (Post Cured 4 Hours at 400°F). Note total absence of an exotherm in the 260°C region.

This work raises one fire fighting concern for aircraft with large amounts of these graphite composites. With air (oxygen) present and a now identified exothermic pyrolysis reaction there is a need during the quenching of a fire to reduce the temperature well below 300°C throughout the structure. If this is not done, it is entirely conceivable that bulk heat transfer could initiate the pyrolysis reactions deep in the composite structure. Thus initiated and with increased oxygen from the atmosphere a smoldering fire could be maintained. The experimental activation energies reported here are on the low side for chemical reactions. Thus reaction can be initiated relatively easily.

Further work is needed to quantitatively identify the major pyrolysis products and thus gain insight into the reaction mechanism. Also the effects of air need to be evaluated.

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